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Precision polymers: a kinetic approach for functional poly(norbornenes)[†]

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The potential control over monomer sequence in the ring-opening metathesis polymerization of functional norbornenes is explored based on the difference in reactivity of *endo* and *exo* isomers. This kinetic approach allows the rapid consumption of the *exo*-norbornene and insertion onto the growing poly(norbornene) chain within a narrow region of the overall polymer chain, whilst maintaining a homogeneous backbone. We herein demonstrate that this can be achieved using a range of functional monomers easily derived from commercially available precursors while their polymerization is carried out in a controlled manner.

Introduction

Efforts to synthesize sequence-controlled polymers are dedicated towards replicating the complex, yet precise, structures of macromolecules found in nature. It is anticipated that achieving even a fraction of nature's precision will lead to materials with finely tunable properties and functions.^{1,2} As much as these are extremely wide-ranging, they are all derived from subtle variations in the sequence of only a few building blocks. Whilst synthetic polymers are not a recent development, the progress in defined structures, compositions and sequences has been immense over the past few decades with the introduction of controlled polymerizations that allow the synthesis of complex copolymers such as block, graft, alternating and gradient materials.³

Techniques that allow the sequential polymerization of functional monomers in a precise manner are still, however, somewhat limited.⁴ Exact control over the macromolecular sequence in polymeric materials tends to involve step-growth processes, whereby sequences are the result of the addition of one – and only one – monomer unit on the growing chain end by an iterative addition–activation process. Such processes include esterification,⁵ nitron-mediated radical coupling,⁶ amidation,^{7,8} Horner–Wadsworth–Emmons (HWE) chemistry,⁹ Wittig olefination,¹⁰ the Passerini reaction,¹¹ thiolactone chemistry¹² and azide–alkyne Huisgen cycloaddition.¹³ A one-pot method was recently reported where the polymer consisted of a repeated short sequence that was first synthesized *via* a combination of organic reactions.¹⁴ While these step-growth approaches are highly reliable in terms of absolute sequence control, they are

limited to the production of oligomers due to the complexity of the synthetic procedures and the cumulative effects of imperfect coupling, while the disproportionate high cost and poor product yield adds to the disadvantages. Perhaps the most efficient and widely used such technique is solid phase peptide synthesis,^{7,15} whereas other elegant approaches to sequence control, such as DNA templating,^{10,16} significantly suffer from scale and cost issues. This is a considerable drawback when contemplating the use of such methods for the exploration of materials with properties derived from their sequence.

A few attempts to harness control of the sequence in addition polymerizations (typically radical processes) can be found in the literature,¹⁷ but perhaps the most extensive study on “precision polymers”² – that is macromolecules whose structure is more sharply defined than typical (co)polymers – has been conducted over the past few years by Lutz and co-workers.¹⁸ By taking advantage of the high reactivity of *N*-substituted maleimides towards styrenic monomers during their radical polymerization,¹⁹ a series of functionalities have been incorporated into a polystyrene backbone in a sequential manner. This strategy has been employed for the synthesis of polymers with a variety of pendent functionalities²⁰ as well as to achieve more complex structures (*i.e.* graft, branch, dendritic polymers).²¹ Indeed, more recently Chan-Seng *et al.* have shown the possibility of further controlling the sequence of the polymer using automated synthetic protocols.²² These kinetic approaches are bridging the gap between selective and precise introduction of reactive functionalities and scalable and readily accessible polymeric materials. However, one fundamental drawback of the use of the styrenic–maleimide pair is the statistical, if not alternating,²³ rather than precise monomeric, incorporation of the functional (maleimide) monomer at low conversion regimes of the auxiliary (styrenic) monomer; a solution to which has been shown to be time-controlled consecutive feeds of the two monomers, but one which adds a further layer of complexity to the synthetic approach.²⁴

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Ring-opening metathesis polymerization (ROMP) is a controlled polymerization method,²⁵ the simplicity and versatility of which has allowed its use in industrial processes.²⁶ In terms of available monomers, ROMP has been most successful with strained cyclic olefins, a major group of which are norbornenes (including oxa- and aza-norbornenes).²⁷ While norbornene derivatives are easily synthesized bearing virtually unlimited possible functionalities, ROMP in the presence of certain functionalities is challenging due to catalyst poisoning and subsequent termination of the polymerization.²⁸ Undeniably, the ability to synthesize nearly monodisperse polymers and complex architectures relies on the range of powerful catalysts available. These have allowed the synthesis of almost perfectly alternating copolymers based on the thermodynamically driven selective bond formation between the explored monomers.²⁹ While these examples demonstrate the potential of ROMP in its use towards the synthesis of sequence-defined polymers, they are limited by the choice of monomer pairs and they often suffer from broad molecular weight distributions.

It has been shown that while *exo*-norbornenes rapidly undergo ROMP in the presence of ruthenium-based catalysts, *endo*-norbornenes exhibit far slower polymerization kinetics attributed primarily to steric interactions between the growing polymer chain and the incoming monomer.³⁰ This has hereinto been perceived as a drawback to using an *endo/exo* monomer mixture as the overall polymerization rate decreases relative to a pure *exo* monomer feed,³¹ however we propose taking advantage of the slow polymerization of *endo*-norbornenes by using them as the auxiliary monomer in precision polymer synthesis. The introduction of a pure *exo*-norbornene monomer into the polymerization reaction should therefore result in its rapid insertion onto the growing polymer chain without otherwise altering the overall *endo* reaction rate. Given that the addition of *exo* monomers does not affect the “living” nature of the polymerization, this should achieve a short sequence of incorporated *exo* monomers at a specific position along the chain. In terms of exploring the material properties of precision polymers, a significant advantage of this system is the homogeneous copolymer backbone, due to the fact that the generic *endo* and *exo* monomers are stereoisomers.

In order to assess the relative polymerization rates of *endo*- and *exo*-norbornenes, *N*-hexyl-*endo*-norbornene-5,6-dicarboximide (*endo*-HexNb) was used as the auxiliary monomer and was copolymerized with three batches of 7-coumarinyl-*exo*-5-norbornene-2-carboxylate (*exo*-CounNb) utilizing Grubbs' 1st generation catalyst in chloroform at room temperature.† At different conversions of *endo*-HexNb, *exo*-CounNb was introduced into the reaction mixture and the progress of the polymerization was monitored by ¹H NMR spectroscopy (Fig. 1). It is apparent that despite the overall reaction being an *exo-endo* copolymerization, which might be expected to negatively affect the polymerization rate,³¹ *exo*-CounNb is consumed significantly faster than *endo*-HexNb. From the slopes of the regression lines of the $\ln([M]_0/[M])$ plots, the apparent polymerization rates (k_{app}) at different *endo* monomer conversions were determined. The overall polymerization rate of the *endo* monomer was found to be $2.68 \times 10^{-6} \text{ s}^{-1}$, and the obtained values for the

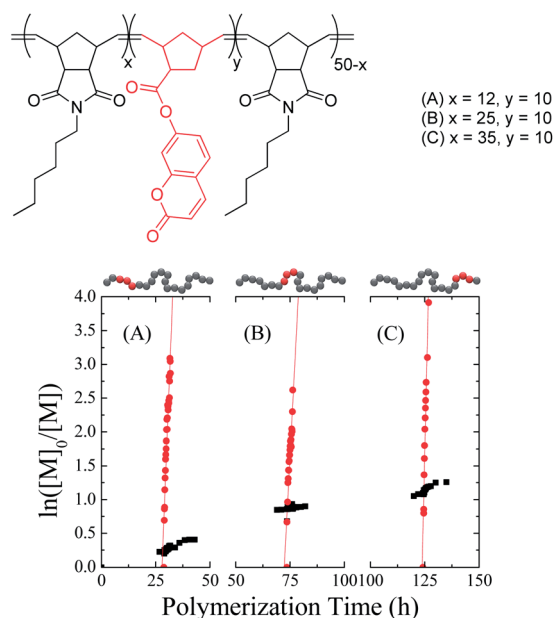


Fig. 1 Chemical structure of the three copolymers (top) and relation between $\ln([M]_0/[M])$ and polymerization time (bottom) for the copolymerization of *endo*-HexNb (squares) and *exo*-CounNb (circles) in CDCl_3 at room temperature at three homopolymerization regimes: (A) 25%, (B) 50% and (C) 70% conversion of the *endo* monomer.

exo monomer were found to be $2.26 \times 10^{-4} \text{ s}^{-1}$ at low *endo* monomer conversion (25%), $1.72 \times 10^{-4} \text{ s}^{-1}$ at 50% *endo* monomer conversion and $3.88 \times 10^{-4} \text{ s}^{-1}$ at higher conversion (70%), ~ 100 times faster. This demonstrates that the rate of polymerization for the *exo*-CounNb is independent of the conversion of *endo*-HexNb at which it was copolymerized, suggesting that precise insertion is possible throughout the polymerization.

A key issue that needs to be addressed when contemplating sequence control is the ability to insert the selected functionality on all growing polymer chains, while controlling the average equivalents added on each chain. To investigate how successful this was in the ROMP case, *endo*-HexNb was again used as the auxiliary monomer and *exo*-CounNb as the functional monomer, one equivalent of which was inserted into the same polymer backbone at four different positions. The use of a coumarin-functionalized norbornene as the functional monomer provides a useful UV handle for characterization of the resultant copolymers. A sample was removed from the polymerization mixture before and after each addition of *exo*-CounNb and was characterized by ¹H NMR spectroscopy and SEC (size exclusion chromatography) analysis. Fig. 2 shows the progression of the molecular weight of the resultant copolymers with reaction time. The overall molecular weight increases and the molecular weight distribution decreases over a period of 355 h in a manner consistent with controlled/“living” polymerizations, suggesting that the polymerization kinetics and control of the auxiliary *endo*-norbornene are unperturbed by each single addition of the *exo*-norbornene.

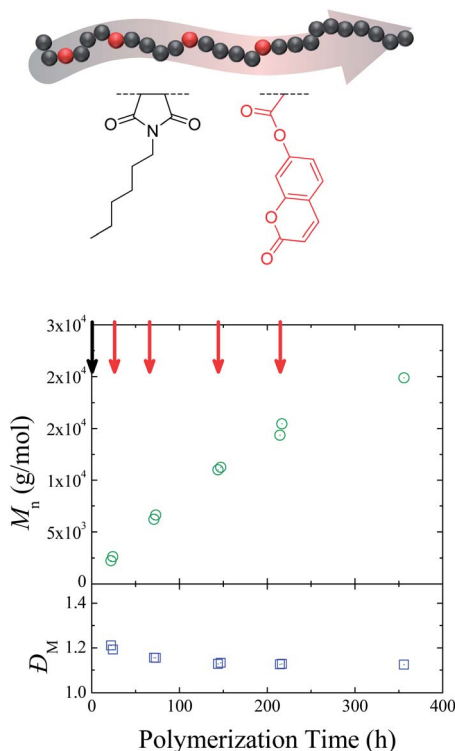


Fig. 2 Chemical structure (top) and evolution of number-average molecular weight (M_n) and molecular weight distribution (D_M) as a function of polymerization time (bottom) for the poly(*endo*-HexNb-*co*-*exo*-CoumNb). Red arrows denote single *exo* monomer addition.

Fig. 3A shows the SEC traces of the final polymer ($M_n = 19\,900\text{ g mol}^{-1}$, $D_M = 1.12$) using both a UV detector measuring the coumarin absorbance at 309 nm and a differential refractive

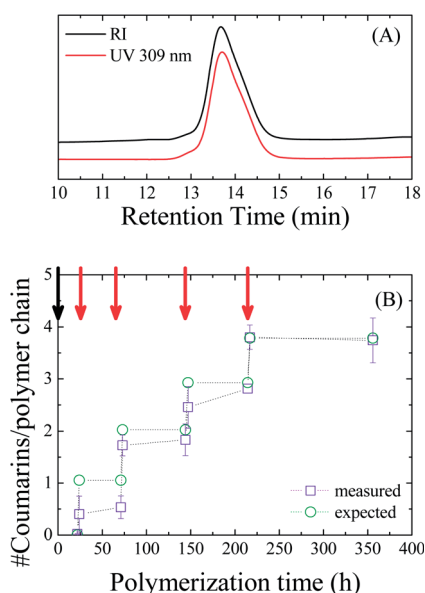


Fig. 3 SEC traces of the final sample using a differential refractive index detector and a UV detector at 309 nm (A) and calculated amount of coumarin moieties per polymer chain vs. polymerization time (B) for the poly(*endo*-HexNb-*co*-*exo*-CoumNb) with addition points of a single *exo* monomer indicated by the red arrows.

index detector. Both traces exhibit identical distributions, which is indicative of successful incorporation of coumarin moieties in all growing polymer chains.

That being established, we attempted to quantify the average amount of coumarin moieties incorporated after each addition of *exo*-CoumNb by measuring UV-vis absorption spectra of the copolymer samples in CH_2Cl_2 (Fig. S3†). The concentration of coumarin in each sample was calculated based on the maximum coumarin absorption (between 310 and 320 nm) and was correlated to the overall polymer concentration. Fig. 3B shows the calculated average number of coumarin moieties per polymer chain with respect to polymerization time as calculated from the UV-vis measurements and is compared to the anticipated amount from the ratio of *exo*-CoumNb to the catalyst present in the reaction mixture. Ideally, after each monomer addition the ratio increases by one, thus suggesting the incorporation of one coumarin moiety per polymer chain on average. While at the initial stages of the polymerization the average coumarin content per polymer chain is low, suggesting incomplete incorporation of the *exo* monomer, upon the last addition, the measured average reaches the expected number of coumarin moieties per polymer chain. While this confirms that the average amount of *exo* monomers inserted per growing polymer chain is controlled, it also shows that the precision with which that monomer is inserted is limited. Further investigations into the factors that dictate the precision of the insertion will focus on the *exo* monomer steric shielding and the mechanistic aspects of cross-polymerization.

The versatility of ROMP in terms of synthesizing precision polymers was assessed by the sequential addition of four different functional *exo*-norbornenes (2 eq. each) in the polymerization mixture of *endo*-HexNb at different monomer conversions. The simplicity of the monomer synthesis afforded the selection of four *exo*-norbornenes bearing diverse functionalities to provide the polymer with unique properties: pentafluorophenyl *exo*-5-norbornene-2-carboxylate (*exo*-PFPNb), (1-pyrenyl)methyl *exo*-5-norbornene-2-carboxylate (*exo*-PyrNb), (trimethylsilyl)methyl *exo*-5-norbornene-2-carboxylate (*exo*-TMSNb) and the previously mentioned *exo*-CoumNb. The incorporation of each functionality into the growing polymer chain was monitored by ^1H NMR spectroscopy while the polymerization rates were calculated from the slopes of the regression lines of the $\ln([M]_0/[M])$ plots (Fig. 4A). Fig. 4B shows the SEC traces of the final polymer ($M_n = 7750\text{ g mol}^{-1}$, $D_M = 1.16$) using a UV detector measuring the coumarin absorbance at 309 nm and the pyrene absorbance at 344 nm as well as a differential refractive index detector. All traces exhibit identical narrow distributions, suggesting good control of the polymerization as well as the presence of both coumarin and pyrene moieties in all growing polymer chains.

Once again, the overall polymerization rate of the auxiliary *endo* monomer was low while each *exo*-norbornene was copolymerized significantly faster. Interestingly, the k_{app} of *endo*-HexNb was found to be $1.43 \times 10^{-5}\text{ s}^{-1}$ which is higher than in our previous experiments, and the k_{app} of the *exo*-norbornenes were found to be $4.16 \times 10^{-4}\text{ s}^{-1}$ for *exo*-PFPNb, $2.12 \times 10^{-3}\text{ s}^{-1}$ for *exo*-TMSNb, $6.56 \times 10^{-4}\text{ s}^{-1}$ for *exo*-PyrNb and $6.94 \times 10^{-4}\text{ s}^{-1}$



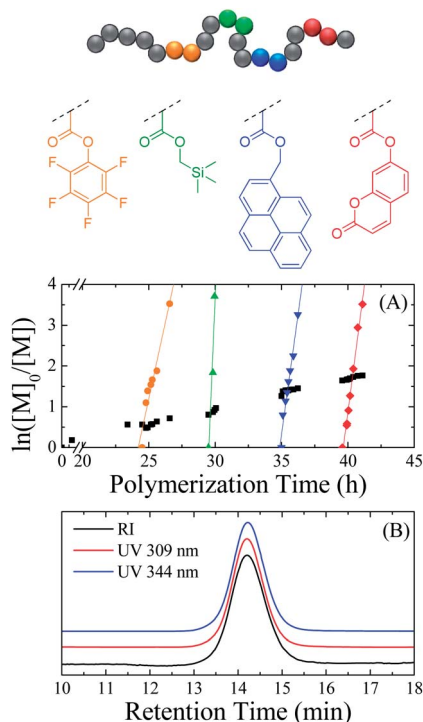


Fig. 4 Relation between $\ln([M]_0/[M])$ and polymerization time (A) and SEC traces of the final copolymer using a differential refractive index detector and a UV detector at 309 nm and 344 nm (B) for the copolymerization of *endo*-HexNb and *exo*-norbornenes with different functionalities.

for *exo*-CounNb which is lower than previously seen. This is possibly a result of the different relative concentrations of the reagents – *i.e.* while the *endo*-norbornene concentration is comparable, the catalyst concentration is higher whereas the *exo*-norbornene concentration is lower. It should also be noted that *exo*-TMSNb exhibited a significantly higher polymerization rate compared to the other *exo* monomers which was attributed to the less bulky pendent group and suggests that relative reaction rates could be easily tuned by adjusting the steric bulk of the *endo* and *exo* monomers. Nevertheless, the polymerization of the *exo* monomers was over 30 times faster than that of the auxiliary monomer indicating the successful synthesis of a multifunctional precision polymer through sequential monomer addition.

Conclusions

To conclude, we have demonstrated the synthesis of polymers *via* ROMP with the ability to easily and relatively accurately control the position of functional moieties on the polymer chain, by taking advantage of the vastly different kinetics of *endo*- and *exo*-norbornenes. It was shown that when adding *exo* monomer in small, defined batches to the auxiliary *endo* polymerization, the presence of both monomers had little effect on their respective reactivity as the *endo*-norbornene was consumed 30–100 times slower than the *exo*-norbornene during their copolymerization. The accuracy of the monomer addition

was investigated by sequentially inserting an *exo*-norbornene bearing a UV-active functionality into a growing *endo* chain at the desired polymerization conversions. In addition, we have successfully synthesized a polymer containing four different functionalities at relatively known positions on the backbone. We believe that any isomerically pure norbornenes that can undergo ROMP can be used as building blocks for the synthesis of precision polymers following this method, expanding the library of possible precision polymers. As ROMP is simple to carry out, can be performed with a range of monomer functionalities, results in a homogeneous backbone and is entirely kinetically driven, we believe that this work complements the precision polymer strategy followed by the Lutz group in leading to a new class of materials with programmable compositions.

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Notes and references

† Initial attempts to use two isomers of the same monomer were unfruitful as we found that overlapping signals in the ^1H NMR spectra significantly affected the accuracy with which we were able to analyze the monomer conversion and polymer composition. However, we have been able to confirm that *exo*-HexNb homopolymerization is as efficient as the *exo*-norbornenes shown in the manuscript (see ESI†).

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